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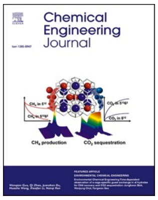

Surfactant changes lead adsorption behaviors and mechanisms on microplastics

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ABSTRACT

The impact of surfactant addition on the adsorption performance of lead ion (Pb^{2+}) as a typical heavy metal ion on three microplastics was investigated. The types of microplastics (polyethylene (PE), polypropylene (PP) and polymethylmethacrylate (PMMA)) and surfactants (triton X-100 (TX-100), 1-hexadecylpyridinium bromide (HDPB), and sodium dodecyl benzenesulfonate (SDBS)), adsorption time, concentration of Pb^{2+}, and coexisting ions was systematically investigated, and the characteristics of adsorption of Pb^{2+} by microplastics were analyzed. The experimental results showed that the adsorption capacity of Pb^{2+} on three micropalstics was different. The adsorption capacity of Pb^{2+} on the three microplastics without surfactants was: 4.21 (PMMA) > 2.01 (PE) > 1.57 mg g^{-1} (PP). The addition of surfactants resulted in a higher hydrophilicity of microplastics, and obviously improved the adsorption ability of microplastics for lead ions. SDBS can significantly enhance the adsorption of Pb^{2+} on three microplastics compared with other two surfactants (TX100 and HDPB). The highest adsorption capacity of Pb^{2+} on the three microplastics with addition of SDBS solution was: 7.87 (PMMA) > 7.20 (PE) > 7.02 mg g^{-1} (PP). With the increase of adsorption time and Pb^{2+} concentration, the adsorption efficiency of microplastics for Pb^{2+} first increased and then decreased. The pH of solution had a great influence on the adsorption of Pb^{2+} by microplastics. The results of coexisting ion experiments demonstrated that when lead ion and copper ion coexist, the two ions have competitive adsorption phenomenon on PP. This research explored the adsorption characteristics of lead ions by microplastics with addition of surfactants, which can provide theoretical basis for further study of heavy metal enrichment and environmental behavior of microplastics in the environment.

1. Introduction

Nowadays, plastic products are widely used in the world, which provides convenience for agriculture, industry, electronic technology and human daily life. The global annual production of plastic products has reached 348 million tons in 2017 and will continue to grow [1–3]. At the same time, the extensive use of plastic products, coupled with improper waste management methods causes the entering of a large amount of plastic wastes into the environment. According to the statistics, 280 million tons of plastic waste were produced in 192 coastal countries and regions around the world in 2011 [4], and about 8 million tons of them flowed into the oceans [5,6]. In the aquatic environment, plastic waste is continuously cracked into fine particles and fragments under the external forces of wind, water shear force, light and biological action [7–9]. These tiny plastic particles seriously threaten the aquatic environment, which not only affect the natural waterscape, but also cause unpredictable hidden dangers to fisheries and navigation safety [10,11]. Additionally, they also hinder the light transmission in water, thereby affecting many biochemical processes [12].

In recent years, microplastic pollution and its ecological effects have become a research hotspot of worldwide concern. Microplastics have high specific surface area because of their small particle size. After corrosion in the aquatic environment, the specific surface area of microplastics further increases. Microplastics are excellent carriers of hydrophobic organic pollutants, heavy metals and microorganisms due to their large specific surface area and strong hydrophobicity [13–15]. Because microplastics are similar to the food of many aquatic organisms, they are easily ingested by aquatic predators. Heavy metals are harmful to organisms even at low concentrations due to their high toxicity and carcinogenic effects [16]. Since microplastics and heavy metals are

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persistent pollutant in the environment, the presence of microplastics can easily transfer heavy metal pollution from one location to another [17]. Microplastics carrying heavy metals eventually enter the human body through the food chain, which is toxic to human health [16].

Lead (Pb) is one of the most common toxic heavy metal pollutants in the global environment [18–21]. Previous studies have shown that microplastics are widespread in the both freshwater and marine environment [22–26]. These two ubiquitous substances may interact in the aquatic environment. The adsorption of Pb^{2+} on microplastics may further change its environmental behaviors, fate, bioavailability and toxicity. Purwiyanto et al systematically studied the concentration and adsorption of Pb^{2+} and Cu^{2+} on virgin microplastics in the aquatic environment [27]. The finding showed that the interaction between microplastics and metals was physical adsorption, and metals can be easily released into aquatic environment through weak bond. In addition, the adsorption capacity of aged microplastics for metals was also studied. Wang et al studied the adsorption behavior of metals in aqueous solution by microplastics effected by UV radiation, and the results demonstrated that aged microplastics had higher adsorption capacity of heavy metals than original ones due to the increased surface area and oxygen containing function after UV radiation [28]. Mao et al also studied the adsorption behavior of mciropalstics aged by UV radiation to heavy metals, and the finding implied also that the adsorption capacity of micropalstics with increasing aging degree because of changes in the physicochemical properties, the roughening of the surface and the appearance of oxygen-containing groups on the surface [29]. Lang et al investigated the Fenton aging affecting the heavy metal adsorption capacity of polystyrene microplastics, and the results indicated that more adsorption sites on microplasic surface were exposed after Fenton aging, physical and chemical adsorption exist simultaneously, and aging microplastics may have a significant effect on the destination and migration of heavy metals in the environment [30]. Wang et al explored the biofilm on microplastics changing the adsorption behaviors of heavy metals and tetracycline, and the findings showed that biofilms on microplastics could enhance the heavy metal migration by changing their adsorption properties on microplastics [31].

The abovementioned studies were to change the adsorption behavior of heavy metals on microplastics through the change of microplastics themselves (aging process) and the enrichment of surface biofilm. Both of them were due to the presence of a large number of oxygen-containing functional groups on the surface of the microplastics. However, limited information is available about the adsorption and desorption characteristics of metals by microplastics in the presence of chemical surfactants. The demand for surfactants is so huge that untreated surfactant wastewater is discharged into the natural water body through various ways [32–34]. At the same time, some surfactants also emulsify other harmful substances, causing an increase in the concentration of these harmful substances [35–37]. It also inhibits the degradation of many toxic chemicals in water, and eventually produces chronic toxic effects on aquatic organisms. Chemical surfactants contain a large number of oxygen-containing functional groups, which can also change the adsorption behavior and migration mode of heavy metals on microplastics. Microplastics are hydrophobic organic pollutants, while the addition of surfactants may change their physical and chemical properties, thus affecting the adsorption characteristics of metals. Therefore, it is important and necessary to study the effect of chemical surfactants on the behavior of microplastics in the environment.

In this paper, the ability of microplastics to adsorb Pb^{2+} in the presence of surfactants was studied. The characteristics of Pb^{2+} adsorption by three kinds of microplastics were systematically studied based on the materials, adsorption time, ion concentrations, kinds of surfactants and surfactant concentrations. The binding mechanism between Pb^{2+} and microplastics was also explored. This research can further clarify the environmental behavior of Pb^{2+} and microplastics coexisting in the aquatic environment. It is of great significance to scientifically and reasonably evaluate the ecological environmental risks of microplastics and heavy metal ions.

2. Materials and methods

2.1. Chemicals and reagents

Polyethylene (PE), polypropylene (PP) and polymethylmethacrylate (PMMA) microplastic powders were obtained from Aladdin Chemical Company (Shanghai, China). Particle sizes of microplastics were characterized by electron- and light microscopy image analysis (Fig. 1). Nonionic surfactant triton X-100 (4-(1,1,3,3-tetramethylbutyl) phenylpolyethylene glycol, TX-100), cationic surfactant 1-hexadecylpyridinium bromide (HDPB) and anionic surfactant sodium dodecyl benzenesulfonate (SDBS) were purchased from Aldrich (USA). Three surfactants were all of analytic grade. These three kinds of chemical surfactants are common surfactants, and they contain hydrophilic groups and long carbon chains, which help to reduce the hydrophobicity of microplastics in aqueous solutions. The chemical formula of three surfactants used in this research was listed at Fig. S1. The critical micellization concentrations (CMC) of TX-100, HDPB and SDBS were 150, 273.6 and 609 mg L^{-1}, respectively [38]. $Pb(NO_3)_2$, $Cu(NO_3)_2$ and concentrated nitric acid are all analytical pure and were purchased from Aladdin Chemical Company (Shanghai, China). Standard solutions of Pb^{2+} and Cu^{2+}, with a concentration of 1000 μg mL^{-1}, were of analytic grade and obtained from Dima (USA). The concentration of three surfactant stock solution was of 10 CMC, and the concentration of lead stock solution was of 200 mg L^{-1}. The water used in the experiments was ultrapure water extracted by Milli-Q pure water mechanism.

2.2. Sorption experiments

2.2.1. Kinetics experiment

All experiments were performed in 20 mL brown glass centrifugal tube. Two concentration gradients of the three surfactants (1 and 5 CMC) and lead solution with initial concentration of 20 and 100 mg L^{-1} were selected. All microplastic particles were thoroughly washed with Milli-Q and 2% HNO_3 solution and dried at 40 °C before use. Ten milligrams of the three treated microplastics and different volumes of lead solution and surfactant solution were added and the final total volume was 10 mL. Eight sampling time points were set (0, 1, 2, 4, 8, 16, 32 and 48 h), and three parallel samples were taken out at each sampling time point. The glass conical flask mouths were sealed with a sealing film, and then placed in a water bath shaker. The rotation speed of the shaker was 150 rpm and the conical flasks were oscillated for 48 h at room temperature (25 °C).

The pseudo-first-order kinetic model and pseudo-second-order kinetic model were used to describe the kinetic adsorption of Pb^{2+} on microplastics [39], and the fitting equations are:

The pseudo-first-order kinetic model:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{1}$$

The pseudo-second-order kinetic model:

$$q_t = \frac{k_2 q_e^2 t}{k_2 q_e t + 1} \tag{2}$$

where q_e (mg g^{-1}) was the saturated adsorption capacity of Pb^{2+} at equilibrium; q_t (mg g^{-1}) was the adsorption capacity at the time of t (h); k_1 (h^{-1}) was the reaction rate constant of the pseudo-first-order kinetic model; and k_2 (g $mg^{-1}h^{-1}$) was the reaction rate constant of the pseudo-second-order kinetic model.

2.2.2. Isothermal adsorption

Batch isothermal adsorption experiments were performed to measure heavy metal sorption onto microplastics in the presence of surfactants. All experiments were carried out in 150 mL glass conical flasks.

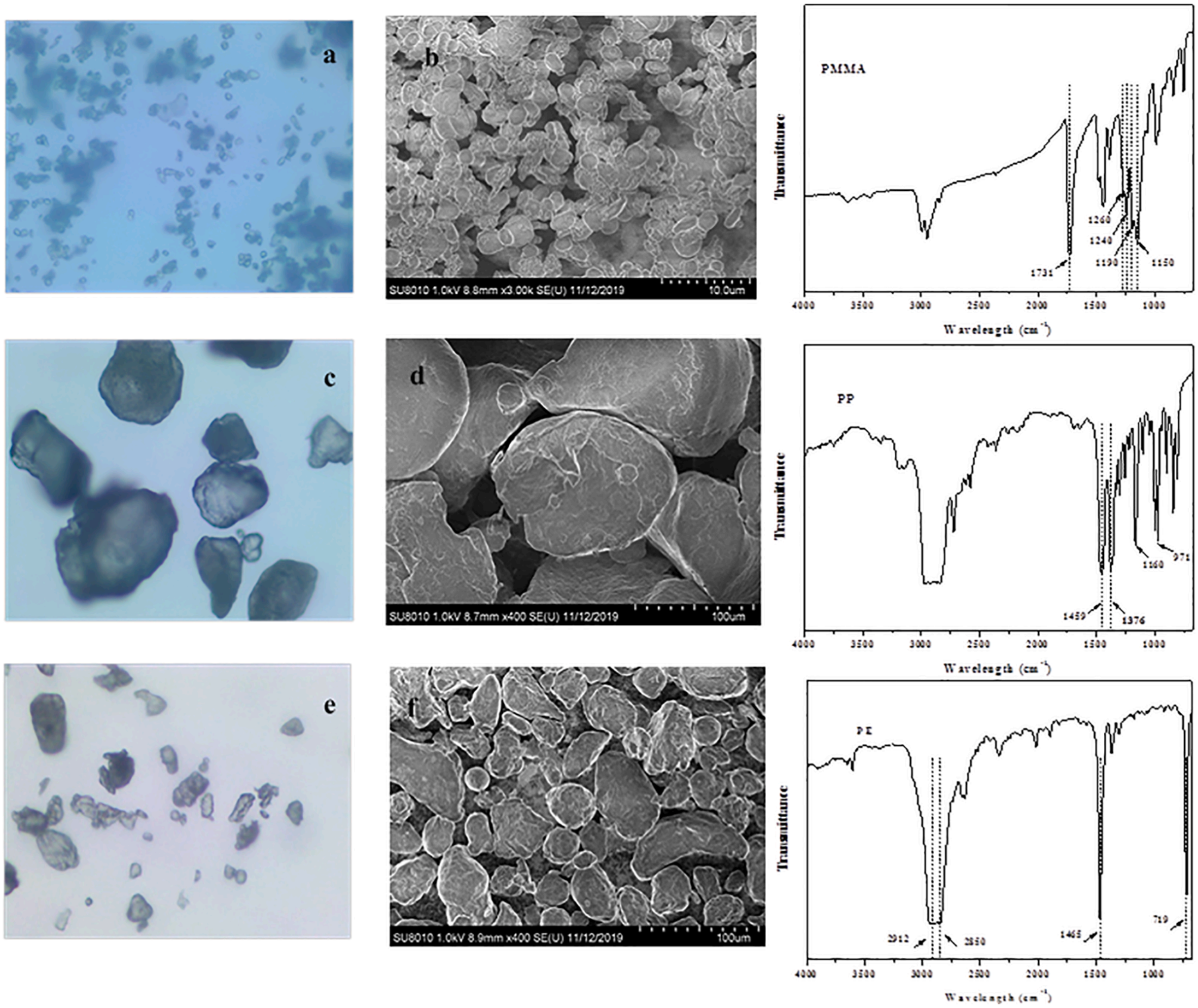

Fig. 1. SEM images of PMMA, PP and PE microplastics.

Eight concentration gradients of Pb^{2+} (0, 1, 2, 5, 10, 20, 50, 100 mg L^{-1}) and seven concentration gradients of the three surfactants (0, 0.1, 0.25, 0.5, 1, 2, 5 CMC) were set up in the isothermal adsorption experiments, and each gradient was set in three parallel groups. 0.10 g of treated micro-PE, PP and PMMA was added into each flask, respectively. According to the concentration gradients, different volumes of Pb^{2+} stock solution, surfactant stock solution and Milli-Q water were added, and the total volume of the final solution in glass conical flask was 100 mL. The glass conical flask mouths were sealed with a sealing film, and then placed in a water bath shaker. The rotation speed of the shaker was 150 rpm and the conical flasks were oscillated for 48 h at room temperature (25 °C). All experiments were repeated three times, and the experimental conditions were the same as abovementioned.

The Langmuir and Freundlich models were used to describe adsorption and desorption isotherms of Pb^{2+} on microplastics, and the fitting equations are:

The Langmuir model:

$$\frac{C_e}{q} = \frac{C_e}{K_1} + \frac{1}{K_1 K_2} \tag{3}$$

The Freundlich model:

$$\log q = \log K_f + \frac{1}{n_f}\log C_e \tag{4}$$

where C_e (mg L^{-1}) was the concentration of Pb^{2+} at equilibrium; q (mg g^{-1}) was the mass of Pb^{2+} adsorbed on unit microplastics; K_f (L kg^{-1}) and n_f represent the strength of adsorption and the degree of nonlinearity of adsorption in the Freundlich model, respectively; K_1 (mg g^{-1}) was the maximum adsorption capacity of Pb^{2+} on microplastics; K_2 (L mg^{-1}) was the index of adsorption energy in the Langmuir model.

2.3. Adsorption under two different conditions

In order to explore the impact of three surfactants on the adsorption of Pb^{2+} on three kinds of microplastics in solution, the order of their addition was tested. Briefly, concentration of each surfactant at the best adsorption effect in isothermal experiments and 20 mg L^{-1} of Pb^{2+} were selected. One group was first added with surfactant and microplastics (first), and the other group was first added with Pb^{2+} and microplastics (second). The glass conical flask mouths were sealed with a sealing film, and then placed in a water bath shaker. Two days later, Pb^{2+} and surfactant were added in different groups, respectively, and then shocked for five days. The oscillation condition is the same as that of isothermal experiment. Each sample was set in three parallel groups.

2.4. Effect of solution pH on the adsorption of Pb^{2+} on microplastic with addition of surfactants

The effect of solution pH on the adsorption of Pb^{2+} on micropalstic with addition of surfactants was performed. The PE microplastics were chosen, and the pH range of the solution was set to 3–11 (3, 5, 7, 9 and 11) in this study. Concentration of each surfactant at the best adsorption effect in isothermal experiments and 20 mg L^{-1} of Pb^{2+} were selected. The glass conical flask mouths were sealed with a sealing film, and then placed in a water bath shaker. All experiments were repeated three times. The experimental conditions were the same as the above release experiment.

2.5. *Effect of coexisting heavy metal ion (Cu^{2+}) on the adsorption of Pb^{2+}*

In order to study the effect of coexisting heavy metal ions on the adsorption of Pb^{2+} on microplastics, the common heavy metal ion Cu^{2+} was selected to prepared the double ion solution system of Cu^{2+} and Pb^{2+} with the each concentration of 20 mg L^{-1}. Two concentration gradients of three surfactants were selected (0 CMC and the concentration of each surfactant at the best adsorption effect in isothermal experiments). 0.1 g of three treated microplastics and a certain of mixed ion solution and surfactant solution were added in a 150 mL glass conical flask, and the final total volume was to be 100 mL. Then the same oscillation treatment as in the isothermal experiments was performed.

2.6. *Sampling process*

After sorption experiments, the microplastic particles adsorbing Pb^{2+} were gathered by 0.45 μm filtration membrane, and then transferred in a 5 mL glass centrifugal tube. Milli-Q water was added to immerse these microplastics for 1 min, and then the detergent was immediately removed. Subsequently, 2 mL of 2% HNO_3 solution were added to the centrifugal tube and ultrasonic-assisted cleaning was carried out with an ultrasonic instrument for 10 min at 120 W at room temperature (25 °C). Finally, the cleaning solution was filtered with 0.45 μm filtration membrane and the filtered solution was used for testing.

2.7. *Chemical analysis and characterization*

Brunauer-emmett-teller (BET) surface area analysis, scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), μ-fourier transform infrared spectroscopy (μ-FTIR), and X-ray photoelectron spectroscopy (XPS) were used to characterize the adsorbents. The content of Pb^{2+} adsorbed by microplastics was determined by Agilent Atomic Absorption Spectroscopy. Microplastic samples before and after adsorption were treated by freeze-drying. After freeze-drying, the microplastic samples were pressed on the surface of diamond crystals and analyzed qualitatively by μ-FTIR. The spectral range was set to 4000–675 cm^{-1}, and the spectral resolution was set to 6 cm^{-1}. The number of scans was 16 times and the data interval was 0.482 cm^{-1}.

3. Results and discussions

3.1. *Characterization of PMMA, PP and PE microplastics*

The adsorption of Pb^{2+} on microplastics is closely related to the surface morphology and structure of microplastics. The optical microscopy images of virgin microplastics were shown at Fig. 1a, c, and e. The morphology of all three microplastics (PMMA, PP and PE) was irregular. The surfaces of these microplastics were further characterized by SEM and presented in Fig. 1b, d, and f. The mean particle size of PMMA, PP and PE microplastics was 6.3, 85.4 and 286.7 μm, respectively. The surfaces of three kinds of microplastics were rough, and there were many pores. Compared with PE, the surface of PP was more wrinkled and less smooth. SEM results showed that there are more folds and more developed pore structures on the surface of PP particles than that of PE particles (Fig. S2).

3.2. *Investigation of acid desorption*

The desorption effects of acid-ultrasound, acid ultrasound after washing and acid soaking (2% HNO_3) were investigated. The results showed that acid ultrasound after washing has less loss of lead adsorption, better parallelism and less error compared with other two methods (Fig. 2). After water washing, the liquids droplets gathered on the surface of microplastic particles can be reduced and the interference caused by the solution adhering to the surface can be significantly avoided. The results showed that the desorption rate of microplastics adsorbed by acid ultrasonic after water washing can reach >97%. Therefore, acid ultrasound after washing (2% HNO_3, 120 W, 10 min) was chosen as the best desorption method in this paper.

3.3. *Kinetic adsorption*

The kinetic adsorption curves of Pb^{2+} on three microplastics at different initial concentration (20 and 100 mg L^{-1}) with addition of surfactants were illustrated in Fig. 3. The adsorption of Pb^{2+} on microplastics can be divided three parts: fast adsorption period, slow adsorption period and adsorption equilibrium period. Taking PMMA as example, the adsorption of Pb^{2+} on PMMA was >60% of the total adsorption capacity within 6 h from the beginning of adsorption. It can be seen that the adsorption at this stage was a fast adsorption process. With time prolonging, the adsorption rate slowed down, and the adsorption equilibrium was reached by adding TX100 and HDPB until 48 h. However, the adsorption process by adding SDBS maintained a slow growth rate after 48 h, and the equilibrium was not reached. The total adsorption capacity of Pb^{2+} on PMMA was 5.35, 5.03 and 7.87 mg g^{-1} at the initial Pb^{2+} concentration of 20 mg L^{-1} with addition of TX100, HDPB and SDBS, respectively. The addition of SDBS significantly increased the adsorption of Pb^{2+} on PMMA, about 1.56 times as much as that of adding HDPB.

The adsorption process of Pb^{2+} on PMMA at the initial Pb^{2+} concentration of 100 mg L^{-1} also can be divided three parts: fast adsorption period, slow adsorption period and adsorption equilibrium period. The total adsorption capacity of Pb^{2+} on PMMA was 8.24, 7.82 and 35.89 mg g^{-1} with addition of TX100, HDPB and SDBS, respectively. The addition of SDBS obviously increased the adsorption of Pb^{2+} on PMMA, about 4.59 and 4.36 times as much as that of adding HDPB and TX100. Additionally, the total adsorption capacity of Pb^{2+} on PP was 5.96 (8.10), 4.87 (6.30) and 7.02 (24.03) mg g^{-1} and on PE was 3.21 (5.52), 3.15 (5.03) and 7.20 (19.03) mg g^{-1} at the initial Pb^{2+} concentration of 20 (1 0 0) mg L^{-1} with addition of TX100, HDPB and SDBS, respectively. Therefore, according to these data, the adsorption capacity of PMMA for Pb^{2+} was much higher than that of PP and PE, and the enhancement effect of SDBS on Pb^{2+} adsorption was much greater than that of HDPB and TX100.

In order to clarify the adsorption process of Pb^{2+} on three

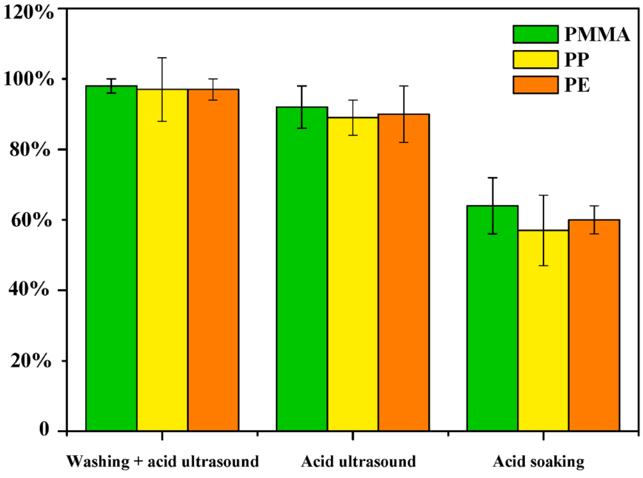

Fig. 2. Effect of different desorption methods on desorption efficiency.

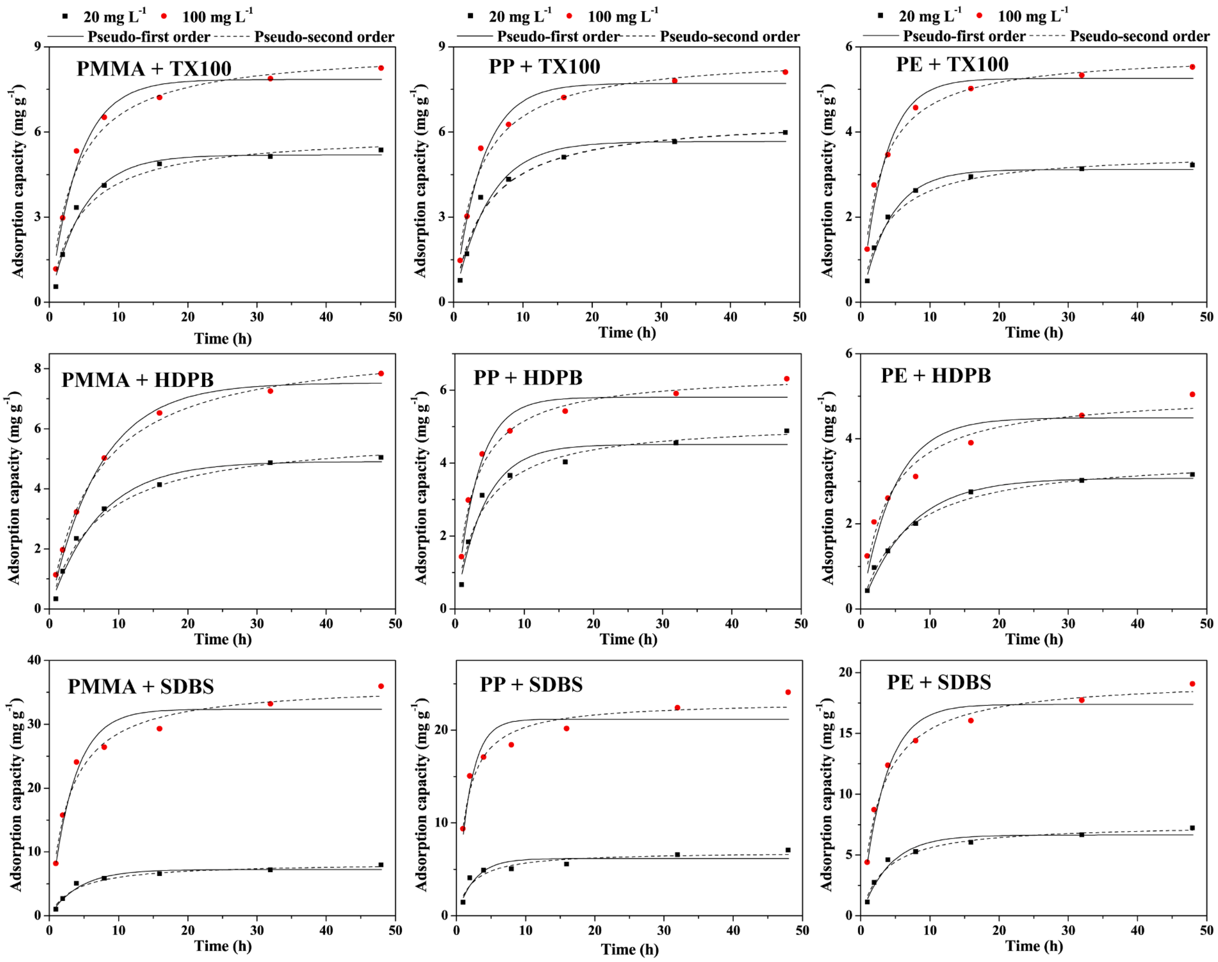

Fig. 3. Adsorption isotherms (Langmuir) of Pb^{2+} on microplastics under different conditions.

microplastics with addition surfactants, the adsorption kinetics data were fitted by pseudo-first-order and pseudo-second-order kinetic equations, respectively (Table 1). Form the Table 1, it can be seen that pseudo-second-order kinetic fitting results are better ($R^2 > 0.89$). When the initial concentration of Pb^{2+} increased, the adsorption rate k_2 decreased, which may be related to the complex adsorption between adsorbate and adsorbent, especially the adsorption of Pb^{2+} on microplastics in the later stage of the adsorption. The adsorption of Pb^{2+} on microplastics may be a multi-phase adsorption process. In the first two stages, the external diffusion and intrapaticle diffusion proceeded rapidly, and in the third stage, the surface diffusion rate at the active site of microplastics was significantly lower than that at the external diffusion site. It can be seen that the third stage of adsorption is the dominant factor affecting the adsorption rate [40]. Additionally, the adsorption rate obviously decreased with the increase of initial Pb^{2+} concentrations. It may be that the increase of the Pb^{2+} concentrations increased the collision probability between molecules, thus prolonging the time of binging Pb^{2+} to active sties of microplastics [41]. Nonionic surfactant TX100 combined with microplastics in solution through hydrophobic chain-chain action, which changed the solubility of microplastics. Lead ions can also be adsorbed on the surface of TX100 by hydrogen bonding [42]. Ionic surfactant (HDPB and SDBS) can interact with microplastics through long carbon chains or electrostatic adsorption. The base band of SDBS head was negatively charged, which also makes the surface of the microplastics negatively charged. Contrary to the charge of Pb^{2+}, the adsorption capacity of Pb^{2+} on microplastic surface was very large due to electrostatic attraction. However, the base band of HDPB head was positively charged, which is the same as that of Pb^{2+}, and the adsorption capacity of Pb^{2+} in the mixed system was small.

3.4. *Isothermal adsorption*

The isothermal adsorption curves can reveal the equilibrium state of adsorbate in solution and adsorbent, and further clarify the occurrence of adsorption mechanism. The isothermal adsorption curves of Pb^{2+} on microplastics at different initial concentrations (0–100 mg L^{-1}), surfactant types and concentrations were illustrated in Figs. 4 and S3. The isothermal adsorption curve of Pb^{2+} showed non-linear adsorption in the whole concentration range, indicating that the distribution of adsorption sites and active groups on the surface of microplastics was not uniform.

The fitting parameters and correlation coefficients were listed in Table 2 (Langmuir) and Table S1 (Freundlich). Langmuir model can better fit these isothermal adsorption curves by comparing the correlation coefficients (R^2), and its R^2 ranged from 0.89 to 1.0 ($p < 0.001$). The fitting effect of Freundlich model was relatively poor, and its R^2 ranged from 0.74 to 0.99 ($p < 0.001$). In the Langmuir model, the condition of K_1 value was the same as that of the maximum adsorption value in the experiment. But in the Freundlich model, K_f value was relatively chaotic, which is inconsistent with the actual situation in the experiment. Therefore, the Langmuir model was most suitable for describe the adsorption of Pb^{2+} on microplastics with addition of surfactants.

The three kinds of microplastics (PMMA, PP and PE) also have the ability to adsorb Pb^{2+} without surfactant, and the adsorption capacity of microplastics for Pb^{2+} was as follows: PMMA (4.21 mg g^{-1}) > PE (2.01 mg g^{-1}) > PP (1.57 mg g^{-1}). The high adsorption capacity of PMMA for

Table 1
Langmuir model parameters of Pb^{2+} adsorption on microplastics with addition of surfactants.

Surfactant type	Surfactant concentration (CMC)	Microplastic type								
		PMMA			PP			PE		
		K_1 (mg·g^{-1})	K_2 (L·mg^{-1})	R^2	K_1 (mg·g^{-1})	K_2 (L·mg^{-1})	R^2	K_1 (mg·g^{-1})	K_2 (L·mg^{-1})	R^2
TX 100	0	4.79 ± 0.27	0.131 ± 0.026	0.97	1.72 ± 0.10	0.211 ± 0.048	0.95	2.23 ± 0.11	0.191 ± 0.036	0.96
	0.1	6.22 ± 0.36	0.080 ± 0.014	0.97	4.30 ± 0.38	0.077 ± 0.021	0.95	2.66 ± 0.20	0.163 ± 0.045	0.94
	0.25	6.68 ± 0.16	0.090 ± 0.007	0.99	4.99 ± 0.24	0.065 ± 0.009	0.98	3.65 ± 0.27	0.076 ± 0.017	0.96
	0.5	7.64 ± 0.31	0.081 ± 0.010	0.98	5.07 ± 0.09	0.067 ± 0.004	1.0	6.58 ± 0.09	0.050 ± 0.002	1.0
	1.0	9.93 ± 0.48	0.059 ± 0.008	0.98	10.36 ± 0.91	0.047 ± 0.011	0.97	4.92 ± 0.14	0.070 ± 0.006	0.99
	2.0	7.43 ± 0.52	0.091 ± 0.021	0.96	6.39 ± 0.20	0.060 ± 0.005	0.99	4.04 ± 0.07	0.086 ± 0.005	1.0
	5.0	6.21 ± 0.47	0.122 ± 0.032	0.95	4.96 ± 0.25	0.049 ± 0.007	0.99	2.44 ± 0.20	0.208 ± 0.066	0.89
HDPB	0	4.79 ± 0.27	0.131 ± 0.026	0.97	1.72 ± 0.10	0.211 ± 0.048	0.95	2.23 ± 0.11	0.191 ± 0.036	0.97
	0.1	4.97 ± 0.09	0.109 ± 0.007	0.98	4.66 ± 0.37	0.080 ± 0.020	0.96	2.42 ± 0.14	0.156 ± 0.034	0.96
	0.25	5.77 ± 0.26	0.114 ± 0.017	0.99	5.45 ± 0.22	0.064 ± 0.008	0.99	3.11 ± 0.09	0.120 ± 0.012	0.99
	0.5	7.04 ± 0.022	0.078 ± 0.007	0.99	6.63 ± 0.37	0.049 ± 0.008	0.98	5.16 ± 0.21	0.049 ± 0.005	0.99
	1.0	9.06 ± 0.02	0.064 ± 0.005	1.0	7.51 ± 0.54	0.065 ± 0.014	0.97	6.42 ± 0.41	0.041 ± 0.007	0.98
	2.0	6.16 ± 0.22	0.096 ± 0.011	0.99	5.78 ± 0.024	0.077 ± 0.010	0.99	3.90 ± 0.12	0.063 ± 0.006	0.99
	5.0	5.35 ± 0.18	0.096 ± 0.007	0.99	4.28 ± 0.24	0.057 ± 0.009	0.98	3.04 ± 0.14	0.067 ± 0.009	0.98
SDBS	0	4.92 ± 0.49	0.111 ± 0.038	0.93	1.72 ± 0.10	0.211 ± 0.048	0.95	2.23 ± 0.11	0.191 ± 0.036	0.97
	0.1	17.77 ± 1.46	0.024 ± 0.004	0.98	6.21 ± 0.48	0.085 ± 0.021	0.92	29.40 ± 5.82	0.011 ± 0.004	0.98
	0.25	26.91 ± 1.88	0.017 ± 0.002	0.99	24.22 ± 1.38	0.020 ± 0.002	0.94	32.34 ± 2.80	0.015 ± 0.002	0.99
	0.5	46.35 ± 7.32	0.010 ± 0.003	0.99	63.24 ± 9.57	0.006 ± 0.001	0.99	37.82 ± 6.97	0.010 ± 0.003	0.95
	1.0	100.84 ± 41.94	0.005 ± 0.003	0.98	48.18 ± 8.82	0.008 ± 0.002	0.93	20.54 ± 1.27	0.019 ± 0.002	0.99
	2.0	105.63 ± 40.91	0.005 ± 0.003	0.98	36.39 ± 5.77	0.010 ± 0.003	0.98	13.70 ± 0.74	0.032 ± 0.004	0.90
	5.0	106.55 ± 41.75	0.006 ± 0.004	0.97	28.78 ± 1.56	0.014 ± 0.001	0.99	11.92 ± 1.57	0.032 ± 0.010	0.96

Pb^{2+} may be due to its small particle size (6.3 μm), high surface area (794.5 m^2 g^{-1}) and large density (1.18 g cm^{-3}). With increase of the concentration of Pb^{2+} in solution, the amount of Pb^{2+} adsorbed on the surface of microplastics increased, and the adsorption rate was fastest between 1 and 5 mg L^{-1}. This may be due to exposure to relatively more adsorption sites at low concentrations. When the concentration was higher than 5 mg L^{-1}, the adsorption rate slowed down because the adsorption mainly occurred on the surface and reached a certain coverage rate affecting the subsequent adsorption.

The surfactant addition significantly increased the adsorption capacity of Pb^{2+} on microplastics. Because of its strong hydrophobicity and low density, microplastics were difficult to get into the solution, but only float on the surface. The addition of surfactants changed the hydrophobicity of microplastics, thus enabling them to fully contact with Pb^{2+}. K_1 in the Langmuir model represents the adsorption capacity of microplastics for Pb^{2+}. The types of surfactants significantly affected the adsorption of Pb^{2+} on microplastics. When nonionic surfactant (TX100) was added, the K_1 value of Pb^{2+} by three microplastics ranged from1.72 ± 0.10 to 10.36 ± 0.91 mg g^{-1}. Analysis of variance showed that there are significance differences in Pb^{2+} adsorption capacity of different types of microplastics under adding TX100 condition ($p < 0.001$). With the increase of TX100 concentration, the K_1 value gradually increased. When the concentration of TX100 was 1 CMC, PMMA and PP had the highest adsorption capacity for Pb^{2+}, reaching 8.12 and 8.15 mg g^{-1}, respectively, which was 1.93 and 5.18 times than that of the case without TX100 (Fig. 3). The maximum adsorption capacity of Pb^{2+} by PE was 5.46 mg g^{-1} (TX100 concentration = 0.5 CMC), which was 2.71 times than that of the case without TX100. In the range below CMC, TX100 existed as a monomer at the interface between solution system and microplastics. The TX100 adsorbed on the surface of microplastics reduced the surface tension and increased the water solubility of microplastics, thus increasing the amount of Pb^{2+} adsorbed on the surface. When the concentration of TX100 continued to increase, the adsorption capacity significantly decreased, which demonstrated that the adsorbed Pb^{2+} was eluted by TX100. In addition, under the same conditions, although the particle size of PMMA and PE was smaller and the specific surface area was larger than PP, the adsorption capacity of PP to Pb^{2+} was higher than that of PMMA and PE (Table 2). The porous properties of PP formed by cross-linking structure enabled PP to adsorb pollutants through surface microporous filling mechanism [43]. The scanning electron microscopy results (Fig. 1) showed that PMMA articles have more wrinkles and pore structures than PE, which help PP to adsorb more Pb^{2+}.

When cationic surfactant (HDPB) was added, the K_1 value of Pb^{2+} on

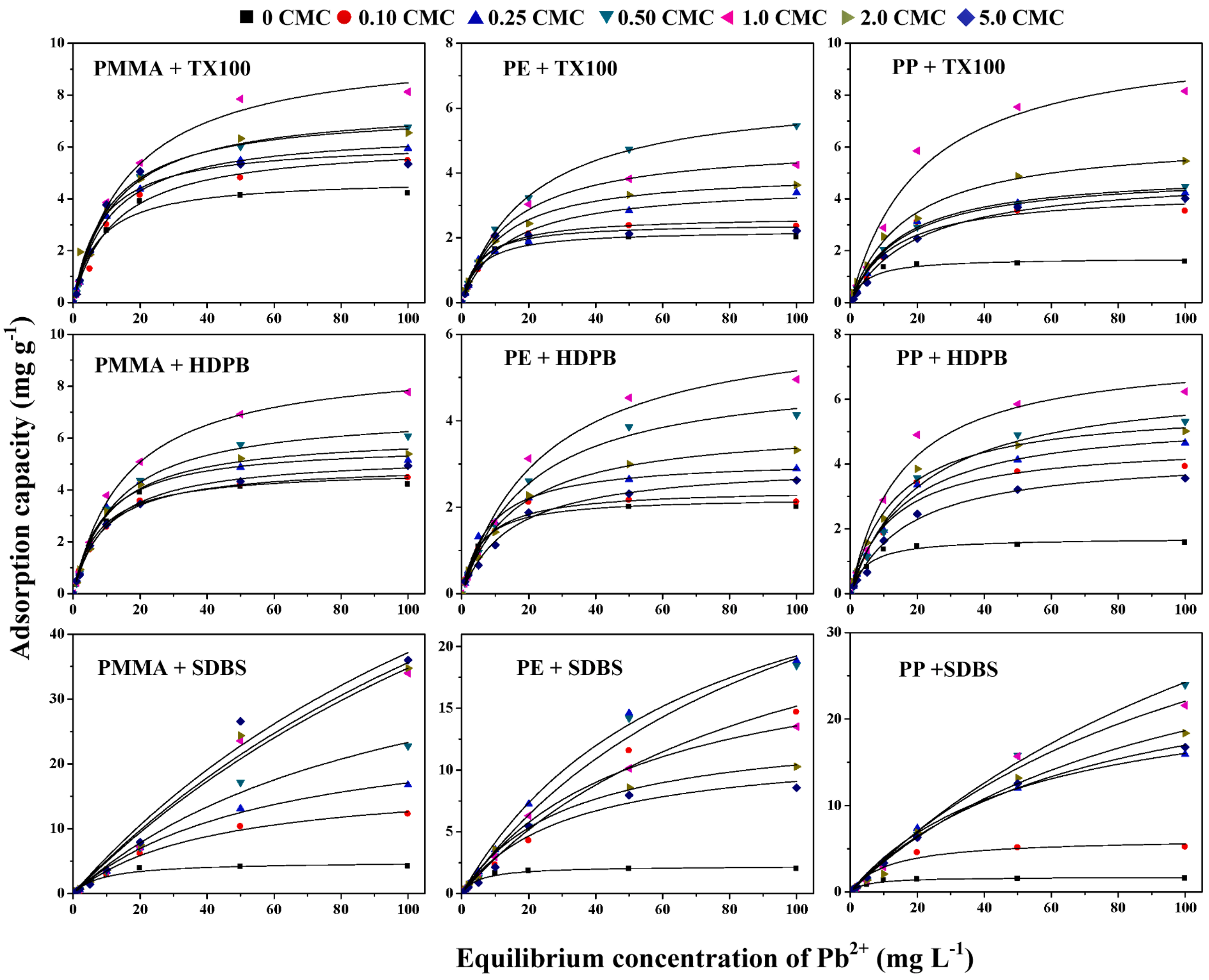

Fig. 4. Mechanisms of Pb^{2+} adsorbed on microplastics by adding different surfactants.

Table 2
Adsorption kinetics fitting parameters of Pb^{2+} on microplastics with addition of surfactants.

Surfactant type	Microplastic type	Concentration of Pb^{2+} (mg·L^{-1})	Pseudo-first-order kinetic model $q_t = q_e(1 - e^{-k_1 t})$			Pseudo-second-order kinetic model $q_t = \frac{k_2 q_e^2 t}{k_2 q_e t + 1}$		
			q_e (mg·g^{-1})	k_1 (h^{-1})	R^2	q_e (mg·g^{-1})	k_2 (g·mg^{-1}·h^{-1})	R^2
TX100	PMMA	20	5.19 ± 0.18	0.206 ± 0.024	0.97	5.96 ± 0.35	0.040 ± 0.007	0.96
		100	7.85 ± 0.25	0.237 ± 0.027	0.97	8.93 ± 0.43	0.031 ± 0.010	0.96
	PP	20	5.66 ± 0.23	0.200 ± 0.027	0.97	6.54 ± 0.35	0.035 ± 0.008	0.96
		100	7.72 ± 0.24	0.250 ± 0.027	0.97	8.73 ± 0.34	0.034 ± 0.006	0.97
	PE	20	3.12 ± 0.07	0.789 ± 0.014	0.99	3.53 ± 0.14	0.081 ± 0.015	0.97
		100	5.26 ± 0.15	0.746 ± 0.023	0.97	5.86 ± 0.18	0.064 ± 0.009	0.98
HDPB	PMMA	20	4.91 ± 0.15	0.138 ± 0.014	0.98	5.85 ± 0.26	0.025 ± 0.005	0.98
		100	7.53 ± 0.15	0.138 ± 0.008	0.99	8.93 ± 0.18	0.017 ± 0.001	1.0
	PP	20	4.51 ± 0.19	0.240 ± 0.036	0.95	5.14 ± 0.25	0.054 ± 0.012	0.96
		100	5.80 ± 0.21	0.311 ± 0.042	0.95	6.48 ± 0.20	0.060 ± 0.009	0.98
	PE	20	3.08 ± 0.07	0.144 ± 0.011	0.97	3.61 ± 0.10	0.045 ± 0.011	0.99
		100	4.49 ± 0.30	0.209 ± 0.048	0.87	5.09 ± 0.24	0.052 ± 0.005	0.96
SDBS	PMMA	20	7.25 ± 0.33	0.230 ± 0.036	0.95	8.30 ± 0.48	0.032 ± 0.008	0.95
		100	32.37 ± 1.47	0.301 ± 0.050	0.93	36.37 ± 1.35	0.010 ± 0.002	0.97
	PP	20	6.17 ± 0.40	0.383 ± 0.098	0.83	6.90 ± 0.46	0.067 ± 0.023	0.89
		100	21.18 ± 1.03	0.535 ± 0.111	0.82	23.13 ± 0.81	0.031 ± 0.006	0.94
	PE	20	6.64 ± 0.28	0.240 ± 0.035	0.96	7.56 ± 0.33	0.037 ± 0.008	0.97
		100	17.39 ± 0.68	0.300 ± 0.042	0.95	19.48 ± 0.54	0.190 ± 0.003	0.98

three microplastics ranged from 2.42 ± 0.14 to 9.06 ± 0.02 mg g^{-1}. Compared with no surfactant addition, the addition of HDPB can significantly increase the adsorption capacity of Pb^{2+} on microplastics.

With the increases of HDPB concentration, the adsorption capacity gradually increased too. When the concentration of HDPB was 1 CMC, three microplastics had the highest adsorption capacity for Pb^{2+}, reaching 7.77 (PMMA), 6.23 (PP) and 4.96 (PE) mg g^{-1}, respectively, which was 1.84, 3.96 and 2.46 times than that of the case without HDPB (Fig. 4). When the concentration of HDPB continued to increase, the adsorption capacity of Pb^{2+} on microplastics significantly decreased. Although the addition of HDPB increased the adsorption of Pb^{2+} on microplastics compared with no surfactant addition, it was less than the adsorption of Pb^{2+} on microplastics when TX100 was added. The K_1 value of Pb^{2+} on three microplastics ranged from 11.92 ± 1.57 to 106.55 ± 41.75 mg g^{-1} with the addition of anionic surfactant (SDBS). The adsorption capacity of Pb^{2+} on PMMA with addition of SDBS continuously increased in the whole SDBS concentration range. However, when SDBS concentration reached 0.5 and 0.25 CMC, the adsorption capacity of Pb^{2+} on PP and PE reached the maximum. According to these results (Fig. 3), we can find that anionic surfactant (SDBS) can significantly enhance the adsorption of Pb^{2+} on three microplastics compared with other two surfactants. The combination of surfactant and microplastics changed the surface charge of microplastics. The mechanisms of Pb^{2+} adsorbed on microplastics by adding different surfactants (TX100, HDPB, and SDBS) were proposed and illustrated in Fig. 5. In TX100/microplastics system, TX100 molecules were adsorbed on the surface of microplastics through carbon chain and hydrogen bond, which increased the adsorption amount of Pb^{2+}. This is mainly because TX100 can not only reduce the water properties of microplastics, but also adsorb Pb^{2+} from aqueous solution by hydroxyl groups on the surface. However, with the increase of its concentration, TX100 molecules in the solution will spontaneously agglomerate into micelles to encapsulate Pb^{2+}, thus reducing the contact with TX100/microplastic system and reducing the adsorption capacity [42]. HDPB molecules were adsorbed on the surface of microplastics by electrostatic and carbon chain interaction, which maked the microplastics also have positive charges [38]. Although its charge was the same as that of lead ion, it can also improve the adsorption capacity of lead at the concentration because it changed the water repellency of the microplastics. However, with the increase of its concentration, more and more positive charges occurred on the surface of the microplastics, the part of Pb^{2+} adsorbed on the solid–liquid interface was replaced by surfactant molecules, which was unfavorable for the adsorption of lead [44]. Additionally, HDPB molecules formed a positively charged micelle sphere, which repels lead ions in the solution. The addition of anionic surfactants made the surface of microplastics negatively charged, which attracts Pb^{2+} in solution system by electrostatic and ionic bonding, thus increasing the adsorption capacity. The negative charged SDBS micelle spheres in the solution also competed to attract Pb^{2+} in the solution, which greatly affected the adsorption on the surface of the microplastics [45]. Finally, the adsorption of Pb^{2+} on microplastics reached the plateau stage in the mixed system.

3.5. Effect of solution pH change on the adsorption of Pb^{2+} on microplastics with surfactants

The effect of solution pH change (3–11) on the adsorption of Pb^{2+} on three microplastics with surfactants was shown in Fig. S4. The pH of solution had a great influence on the adsorption of Pb^{2+} by microplastics. The current results showed that the adsorption of Pb^{2+} by microplastics reached the highest under the neutral or weak alkaline conditions. The maximum adsorption capacity of PMMA for Pb^{2+} was measure to be 5.35 (pH7, TX100), 5.27 (pH9, HDPB) and 8.24 mg g^{-1} (pH9, SDBS) with surfactants, respectively. The maximum adsorption capacity of PP for Pb^{2+} was 9.00 (TX100), 5.54 (HDPB), and 8.22 mg g^{-1} (SDBS) at pH9 with surfactants, respectively. The maximum adsorption capacity of PE for Pb^{2+} was 3.21 (pH7, TX100), 4.72 (pH9, HDPB) and 7.53 mg g^{-1} (pH9, SDBS) with surfactants, respectively. Generally, PMMA has stronger adsorption of lead than PP and PE, which may be related to its properties in solution. The addition of TX100 can only change the surface physical properties, but not the chemical properties. Under the condition of low pH, due to electrostatic repulsion and intermolecular force, the adsorption capacity of HDPB, which was opposite to the surface charge of microplastics, on the surface of microplastics was large, but the adsorption of lead was weakened. However, the base band of SBDS head was negative, and the adsorption amount on the surface of microplastics was less. In addition to enhancing the hydrophilicity of the microplastics, it also increased the negative charge on the surface of the microplastics and had a stronger adsorption capacity for lead. With the increase of pH value, Pb^{2+} could not exist in the form of ions in the solution, and the adsorption capacity of microplastics sharply decreased. The zeta potential of three kinds of microplastics was analyzed and shown in Fig. S5. The potential value of PMMA was negative at all pH conditions, which indicated that PMMA was easily negative in solution. In addition, the potential value of PMMA was much smaller than PP and PE at the same pH, indicating that PMMA had more negative charge. This is consistent with the adsorption trend of Pb^{2+} on microplastics (PMMA > PP > PE).

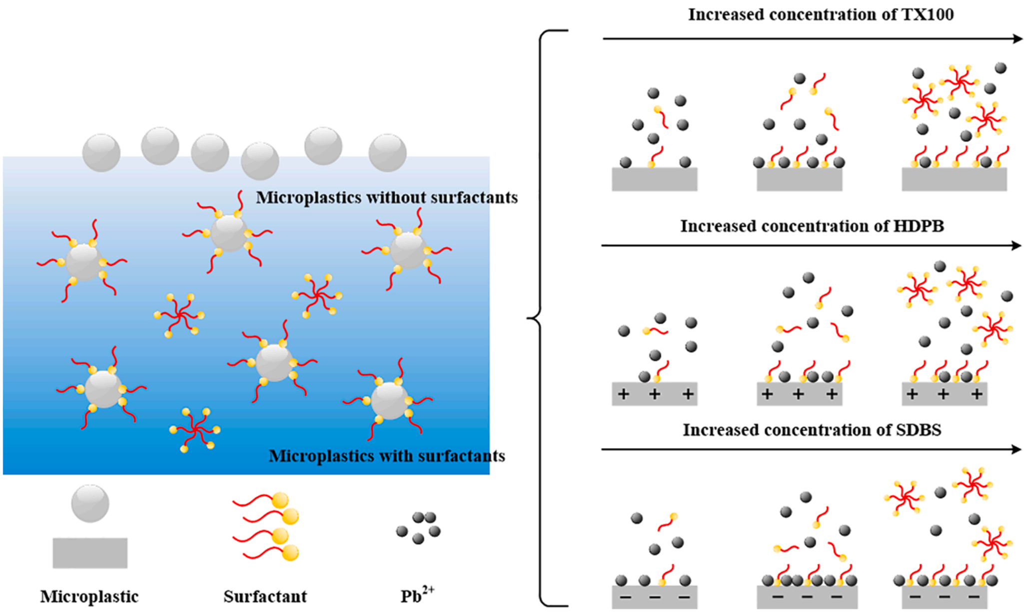

Fig. 5. Effect of initial concentration on the adsorption kinetics of Pb^{2+} on microplastics.

3.6. *Adsorption under two different conditions*

The addition order of microplastics, surfactants and Pb^{2+} could potentially affect the adsorption behavior of Pb^{2+} and further affect their fate in the aquatic environment. As illustrated in Fig. 6, it can be seen that the addition order could affect the adsorption of Pb^{2+} on microplastics (PMMA, PP and PE). In general, the addition order could not influence the total adsorption capacity of Pb^{2+} by microplastics with the increase of reaction time, while the adsorption rate was obviously increased with addition of TX100 and HDPB. The adsorption rate of the first group reaching the adsorption equilibrium was significantly higher than that of the second group. When microplastics and surfactants are added to the reaction system, they can quickly react with microplastics and adsorb on the surface of microplastics because they all have long carbon chains. When Pb^{2+} was added into the system again, the copolymer of microplastics and surfactant had activity (hydrophilic or charged), which can accelerate the adsorption of Pb^{2+} (hydrogen bonding or electrostatic interaction) in the mixed system. In the second conditions, the adsorption sites on the surface of the microplastics will firstly adsorb Pb^{2+} in the solution. While surfactant was added again, it can quickly react with microplastics, which may compete for adsorption sites. However, the addition of SDBS had no significant effect on the adsorption rate, which may be due to the electrostatic and ionic bonding increasing the adsorption capacity.

3.7. *Impact of coexistence ions on Pb^{2+} adsorption*

The common heavy metal ion Cu^{2+} was selected to prepare the two-ion solution system of Cu^{2+} and Pb^{2+} with the each concentration of 20 mg L^{-1}. The selectivity and adsorption volume difference of microplastics with addition of surfactants for Cu^{2+} and Pb^{2+} were illustrated in Fig. 7. At the same concentration, the amount of Pb^{2+} adsorbed by different microplastics in the mixed solution of Cu^{2+} and Pb^{2+} was lower than in the single solution of Pb^{2+}. This showed that the different microplastics have adsorptive properties for all metal ions in the presence of mixed solution. The total adsorption capacity of Pb^{2+} to PMMA, PP and PE was 3.90, 1.47 and 1.82 mg g^{-1} without surfactants in the single Pb^{2+} solution, respectively. But in mixed solution of Cu^{2+} and Pb^{2+}, the total adsorption capacity of Pb^{2+} to PMMA, PP and PE was decreased to 3.74, 0.84 and 1.76 mg g^{-1} without surfactants in the single Pb^{2+} solution, respectively. The decrease of single Pb^{2+} adsorption was mainly due to the competition of Cu^{2+} and Pb^{2+} on the surface of microplastics when two metal ions coexisted. The results showed that the binding ability of Cu^{2+} to PMMA, PP and PE was weaker than that of Pb^{2+}. Because Cu^{2+} is a metal element in the transition zone and has the electronic layer structure of non-inert gas configuration, it is easy to form hydrated ions in aqueous solution, and the strong acid and weak alkalis salts produced at the same time are easy to hydrolyze, thereby affecting the binding ability of Cu^{2+} to microplastics.

In addition, the selective adsorption of Cu^{2+} and Pb^{2+} by different microplastics was quite different. For example, by calculating the number of adsorbed ions, it is found that the number of Pb^{2+} adsorbed by PMMA and PE in a single Pb^{2+} solution was 1.133×10^{19} and 5.288×10^{18} per gram; and in the mixed solution of Cu^{2+} and Pb^{2+}, the number of Pb^{2+} adsorbed by PMMA and PE with the same mass was 1.087×10^{19} and 5.114×10^{18}, respectively. The coexistence of ions had

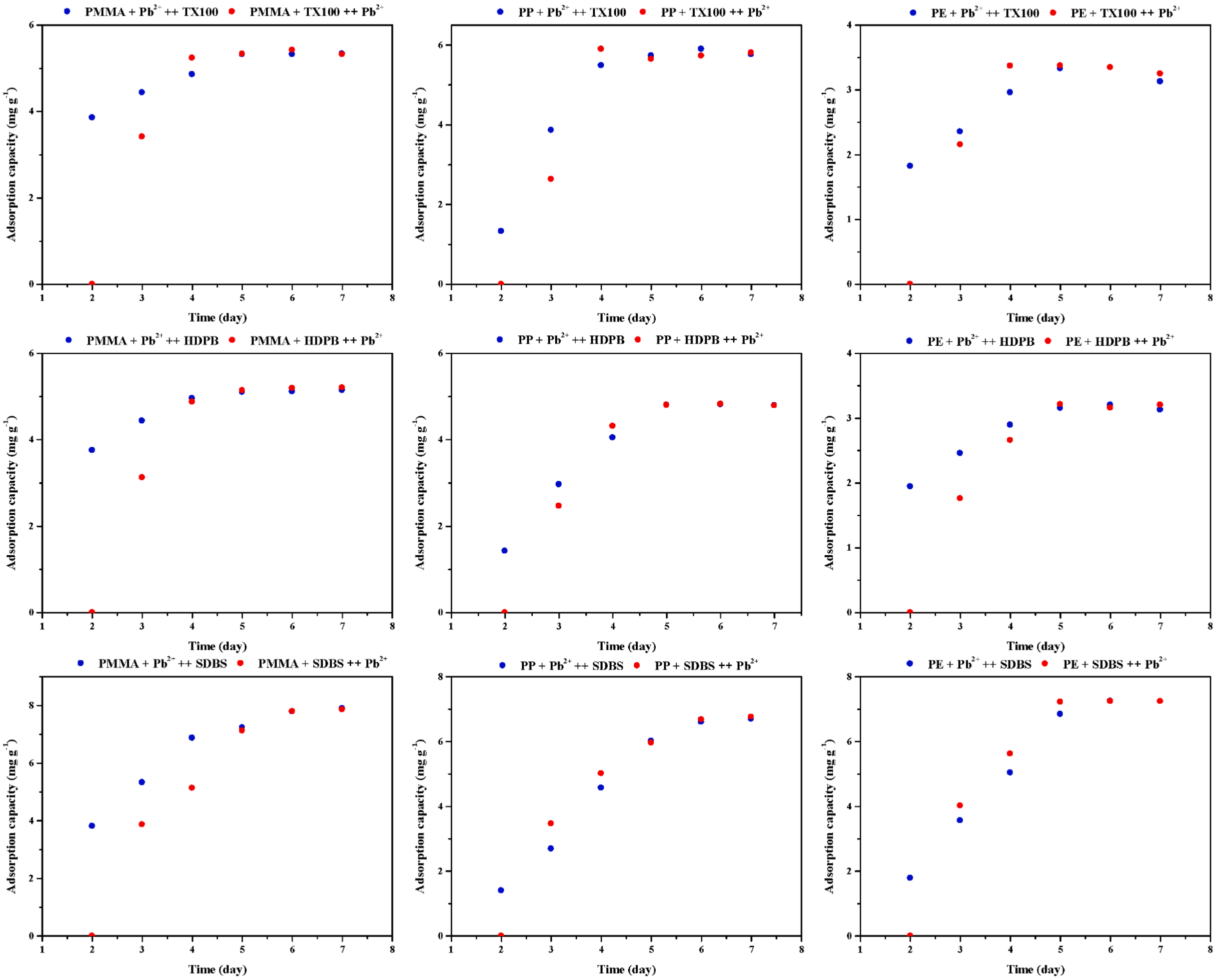

Fig. 6. Effect of adding order of surfactants and Pb^{2+} on adsorption.

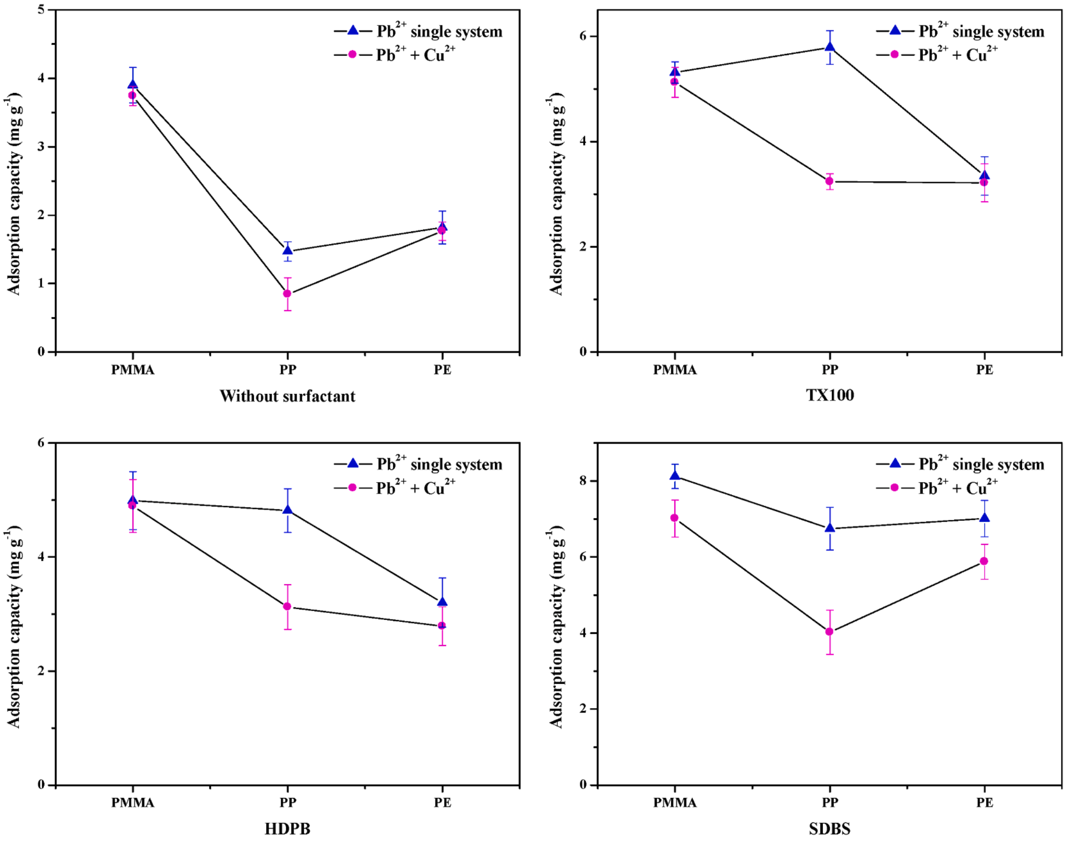

Fig. 7. Effect of coexistence ions on Pb^{2+} adsorption.

little effect on the adsorption of PMMA and PE materials. However, the number of Pb^{2+} adsorbed by PP in the single Pb^{2+} solution system and in the mixed solution system was 4.271 × 10^{18} and 2.440 × 10^{18}, respectively. The results showed that the presence of Cu^{2+} could disturb the adsorption of Pb^{2+}.

3.8. *μ-FTIR and XPS analysis*

The comparison of μ-FTIR spectra of three kinds of microplastics (PMMA, PP and PE) in the wavelength range of 675 – 4000 cm^{-1} before and after Pb^{2+} adsorption with different surfactant addition was illustrated in Fig. 8. It can be seen (Fig. 8A) that the main infrared characteristic absorption peaks of adsorbent PMMA are as follows: the stretching vibration of carbonyl group (C═O) at 1731 cm^{-1} and C-O-C stretching vibration at 1150, 1190, 1240 and 1260 cm^{-1}, respectively. The absorption of PMMA with addition of SDBS is very weak in the region of 1260 – 1150 cm^{-1}, which is different for other three groups. The weak absorption peaks in the region of 1260–1150 cm^{-1} area obviously related to the addition of SDBS surfactant. In the region of 1260–1150 cm^{-1}, the absorption of complex vibration of the combination of C—O—C bond and deformation vibration of different C—O—C is shown. The addition of SDBS in the mixed system decreases the function of C—O—C in PMMA, indicating that the ordered structure of alkyl chain of SDBS surfactant is enhanced on the surface of PMMA microplastics. The changes of these peaks at 1150, 1190, 1240 and 1260 cm^{-1} with addition of SDBS indicate that there may be some chemical adsorption besides physical adsorption for Pb^{2+}.

The significance peaks at 971, 1160, 1376, and 1459 cm^{-1} is contributed by carbon chain of PP microplastics and attributed to rocking deformation, bending deformation, CH_2 symmetric stretching and CH_3 symmetrical deformation vibration, respectively. PP presents characteristic peaks at 971 and 1160 cm^{-1}. Peaks could characterize a lot of functional groups at wavelength range from 1500 cm^{-1} to 675 cm^{-1} (Fig. 8B). The absorption from 1000 cm^{-1} to 950 cm^{-1} region is due to the characteristic coupling of rocking vibration of CH_3 and the vibration of C—C bond. The relatively high peak frequencies of surfactants and PP microplastic indicate that non-ideal mixture between surfactants and PP microplastic and the chain action of hydrophobic agent enhance the ordering degree of alkyl chain on PP microplastic surface. At 719, 1465, 2850 and 2912 cm^{-1}, PE shows different methylene (CH_2) vibration (including in-plane swing vibration, bending vibration, symmetric expansion vibration, asymmetric expansion vibration) and corresponds C—C stretching vibration at 1097 cm^{-1}. Different from the other two surfactants, some new absorption peaks appear at 1130, 1033, 1066 and 833 cm^{-1} in PE and SDBS group (Fig. 8C), respectively, which also demonstrates that chemical adsorption may occur besides physical adsorption during the whole Pb^{2+} adsorption.

In addition, the elemental composition and electronic structure of the microplastics were characterized by XPS. The XPS scans of three experimental plastics were shown in Fig. S6. The C1s spectra of PMMA, PE and PP showed one peak. The main peak was observed at 285–286 eV, corresponding to carbon containing groups: C—C and C—O. The single peak with the maximum value at ~ 532ev appeared in each O1s spectrum of PMMA, PE and PP. There wer no oxygen-containing functional groups in polyethylene and polypropylene molecules, which may be caused by the use of additives. The oxygen-containing groups of COO may be the main factor causing the peak in PMMA. A slight wake associated with the C—O/C—OH group was observed on the left side of the peak. Finally, the N1s spectral region was explored and a peak of 395–400ev was detected, indicating the presence of a nitrogen-containing group (N—C and N═C). The reason for this may be that the HDPB surfactant will be adsorbed on the surface of the microplastics through chemical and physical interaction.

To sum up, in addition to the characteristic absorption peaks of PMMA, PP and PE microplastics, there are some other peaks in the spectrum. Most of the peaks in the spectrum are relatively shifted

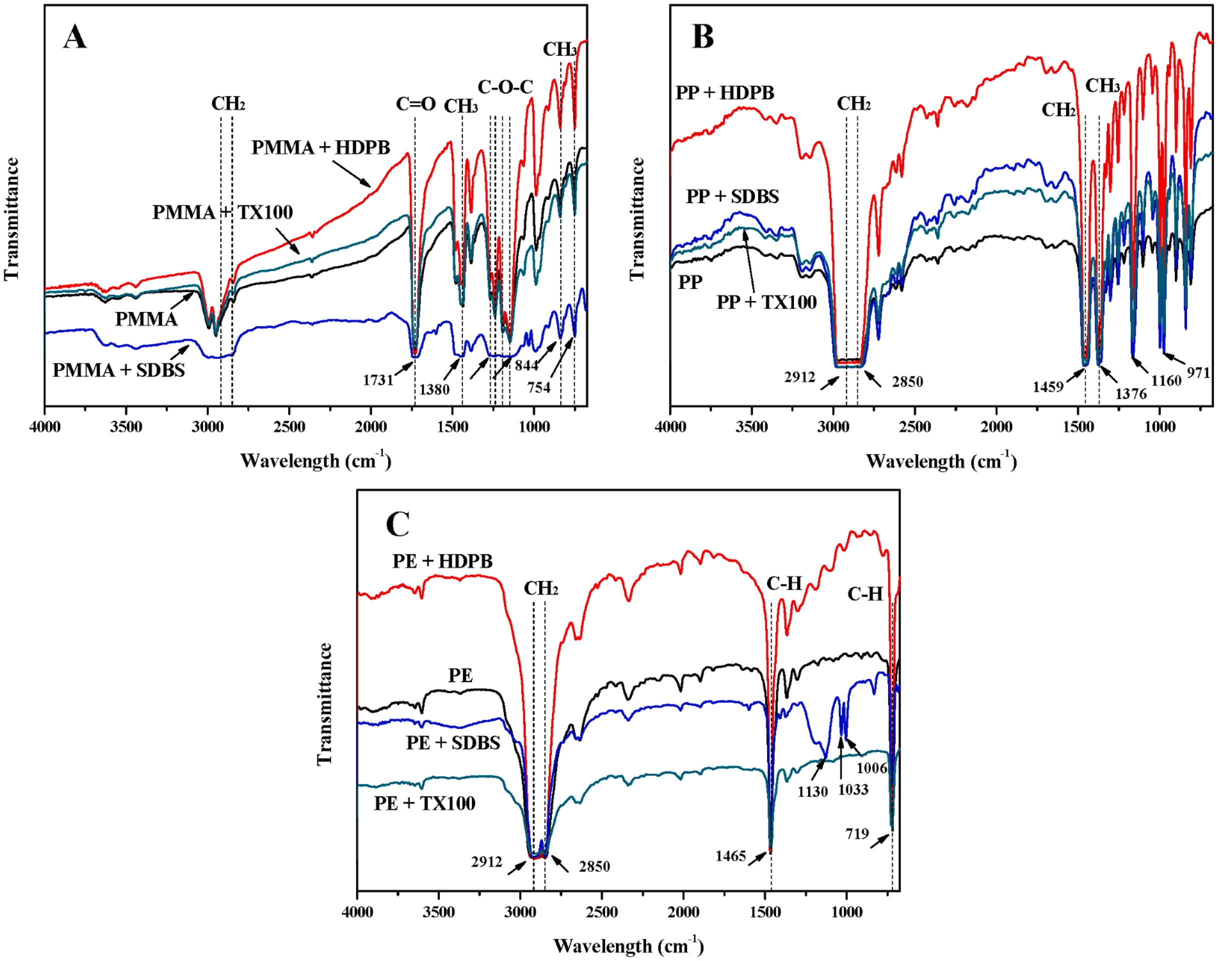

Fig. 8. μ-FTIR spectra for three microplastics.

compared with the original microplastic. Based on the previous studies, it is speculated that the addition of surfactants may be due to the change of the surface of microplastics, forming hydrophilic groups, so as to suspend in water and increases the chance of contact with Pb^{2+} in the solutions. According to the analysis results of the comprehensive spectrum, after the combination of microplastics and surfactants, new groups appear, indicating that there is covalent bond formation in the process of adsorption of surfactants, which proves that surfactants change the characteristics of microplastics.

4. Conclusions

In this study, the effect of surfactant addition on the adsorption performance of Pb^{2+} as a typical heavy metal ion on three microplastics was explored. Different microplastic particles have strong adsorption on Pb^{2+}, but the adsorption capacity of Pb^{2+} on different polymers is different. In the process of adsorption of Pb^{2+} on microplastics, the adsorption capacity was related to time, concentration, particle size and material quality. The adsorption capacity of Pb^{2+} on three kinds of microplastics without addition of surfactants was: PMMA (4.21 mg g^{-1}) > PE (2.01 mg g^{-1}) > PP (1.57 mg g^{-1}). The addition of three kinds of surfactants changed the surface properties of microplastics and the adsorption capacity of Pb^{2+}. The addition of surfactants made the microplastics have better hydrophilicity, and obviously improved the adsorption ability of the microplastics to Pb^{2+}. The highest adsorption capacity of Pb^{2+} on the three microplastics with addition of SDBS solution was: 7.87 mg g^{-1} (PMMA) > 7.20 mg g^{-1} (PE) > 7.02 mg g^{-1} (PP). The adsorption isotherms of Pb^{2+} on microplastics were nonlinear, which can be well fitted by the Langmuir model. The second-order kinetic model can well describe the adsorption kinetics of Pb^{2+} on microplastics. The pH of solution had a great influence on the adsorption of Pb^{2+} by microplastics. The adsorption of Pb^{2+} by microplastics reached the highest under the neutral or weak alkaline conditions. When multiple ions coexist, due to the competitive adsorption of metal ions and the electrostatic effect of surface ions, the adsorption performance of microplasstics for Pb^{2+} will also be affected. The results of μ-FTIR showed that there are some new groups in the adsorption process with addition of surfactant, which demonstrates that some chemical adsorption besides physical adsorption for Pb^{2+} may occur. This study can clarify the environmental behavior of Pb^{2+} and microplastics coexisting in the aquatic environment. It is of great significance to scientifically and reasonably evaluate the ecological environmental risks of microplastics and heavy metal ions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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05).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.126989.

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